한국자기학회 춘계학술대회 (2018.3.30, 강원도 삼척 쏠비치)

Large Thermopower in topological crystalline insulating perovskite $ThTaN_3$

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Collaborations

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➢ **[Acknowledgments]**

- **Y.-K. Kim for discussions on topological insulators,**
- **K.-H. Ahn and Y.-J. Song for technical discussions,**
- **A. P. Ramirez, M. Subramanian, and T. Siegrist for discussions on nitride perovskite.**

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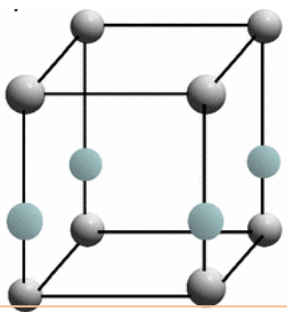
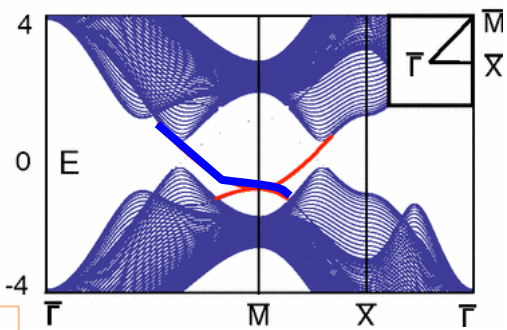
Topological crystalline insulators

C_n + TR sym. in 3D (n=4, 6)

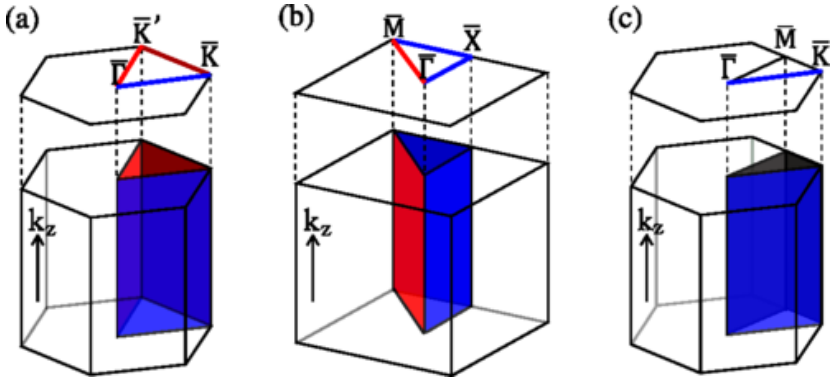




tetragonal lattice

L. Fu (Harvard U.), PRL 106, 016802 (2011).

only C_{nv} (n=3, 4, 6)



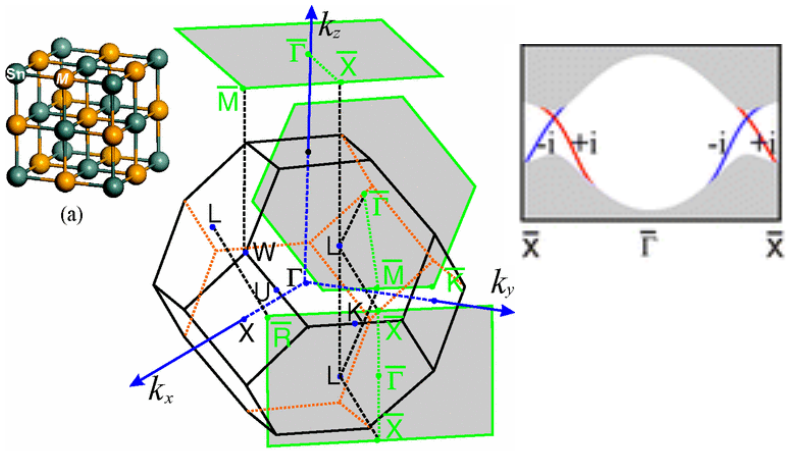
Alexandradinata et al. (Princeton U.), PRL 113, 116403 (2014); PRB 93, 205104 (2016).

- ➢ **TCI**
- ✓ **trivial Z_2 number (cf., Z_2=1 for ordinary Z_2 TIs)**
- ✓ **even crossings in a hybrid Wannier charge center plot**
- ✓ **zero Chern number, but nonzero mirror Chern number**
  [$C_M = (C_{+i} - C_{-i})/2$ for Bloch eigenstates with eigenvalues $\eta = \pm i$]

- ➢ **SOC is not a requirement in TCI, but will affect the gap size.**

Theoretical predictions of TCI

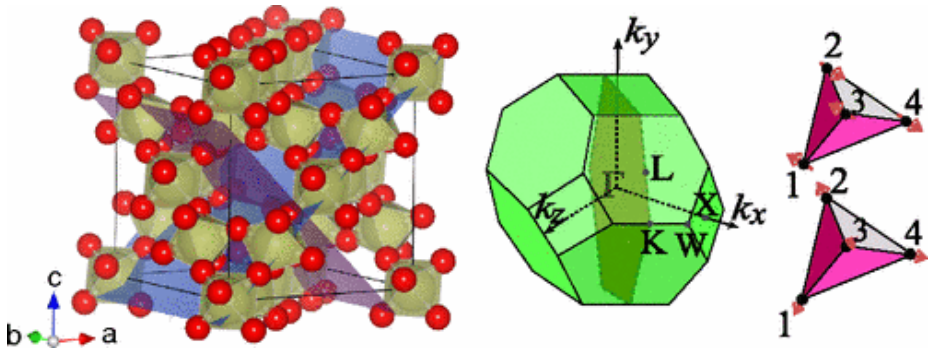
RockSalt IV-VI semiconductor



➢ **Protected by mirror sym.**

- **SnTe, SnS/SnSe**
  Hsieh et al. (MIT), Nat. Commun. 3, 982 (2012);
  Sun et al. (China), Phys. Rev. B 88, 235122 (2013).
- **PbPo**
  Kang and Min (Postech), PRB 93, 041104(R) (2016).
- **Monolayer of PbSe etc.**
  Wrasse and Schmidt (Brazil), Nano Lett. 14, 5717 (2014).
  Liu et al. (MIT), Nano Lett. 15, 2657 (2015).

Transition metal oxides

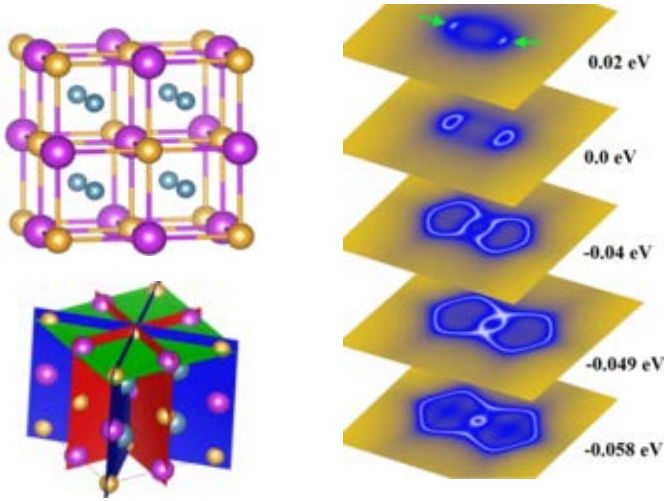


➢ **Protected by mirror sym even for no TR & showing a crucial role of SOC**

- **Pyrochlore oxide $A_2Ir_2O_7$**
  Kargarian & Fiete (U. of Texas, Austin), PRL 110, 156403 (2012)
- **Orthorhombic Perovskite $SrIrO_3$**
  Chen, Lu, & Kee (U. of Toronto), Nat. Commun. 6, 6593 (2015).
- **Antiperovskite**
  Hsieh et al. (MIT), PRB 90, 081112(R) (2014).

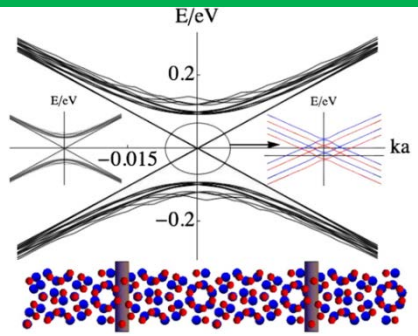
continue

Full-Heusler



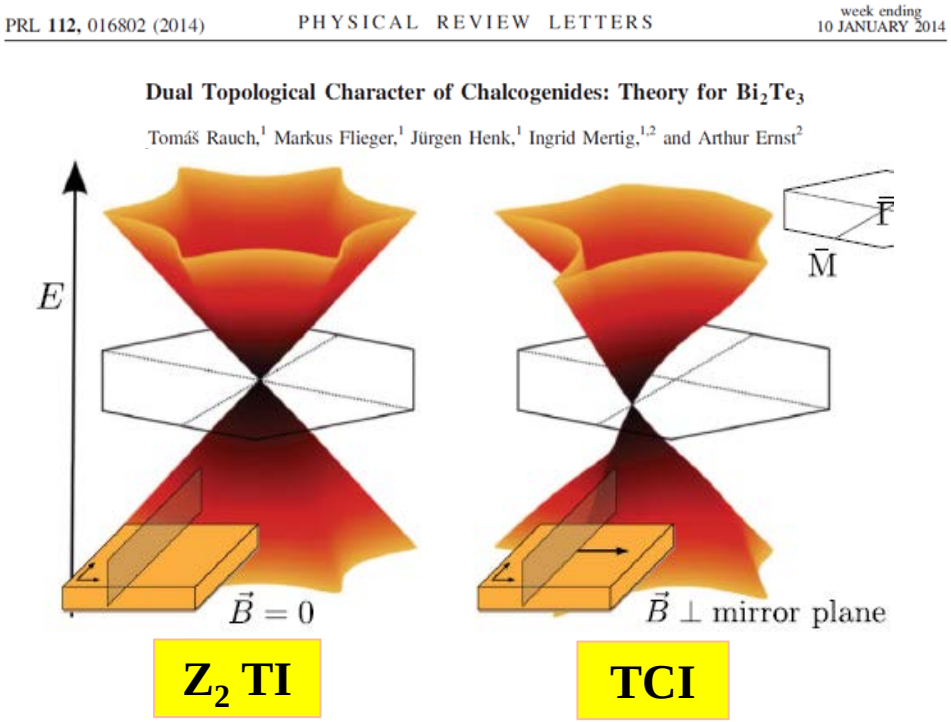
Pham & Li (Australia), PRB 95, 115124 (2017).

Graphen multilayers



Kindermann (Georgia Tech.), PRL 114, 226802 (2015).

- **Note: TCI can coexist with other topological properties.**


PRL 112, 016802 (2014) PHYSICAL REVIEW LETTERS week ending 10 JANUARY 2014

Dual Topological Character of Chalcogenides: Theory for Bi_2Te_3

Tomáš Rauch,[1] Markus Flieger,[1] Jürgen Henk,[1] Ingrid Mertig,[1,2] and Arthur Ernst[2]

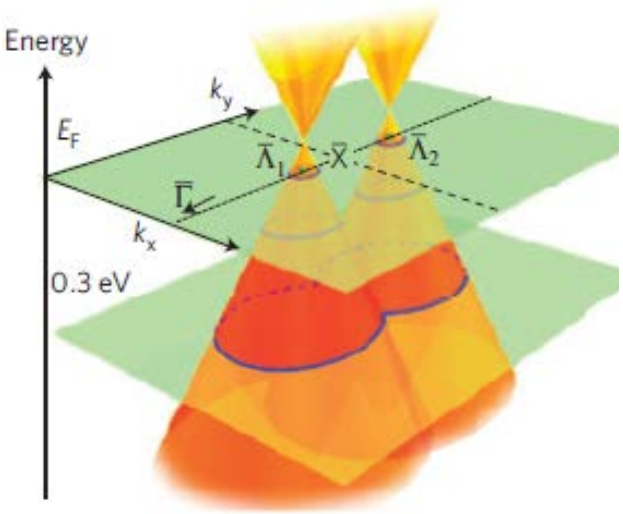
Z_2 TI

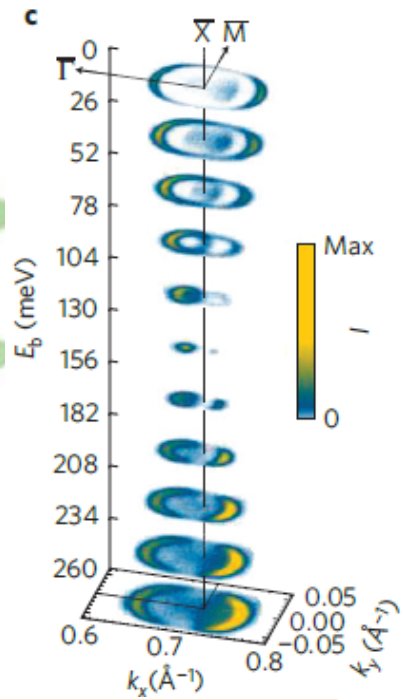
TCI

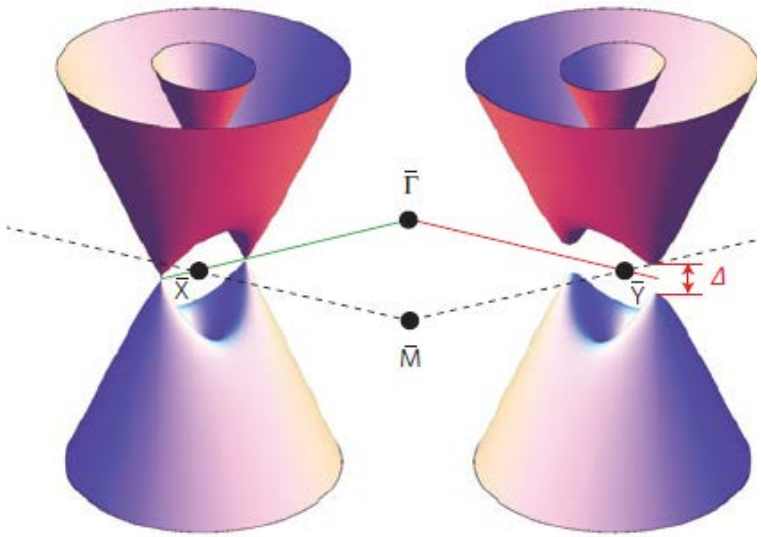
Rauch et al., PRL 112, 016802 (2014).
Rusinov et al., Sci. Reports 6, 20734 (2016).
Munoz et al., Sci. Reports 6, 21790 (2016).

Experimental Observations of TCI

IV-VI semiconductors of (Pb,Sn)Te/Se







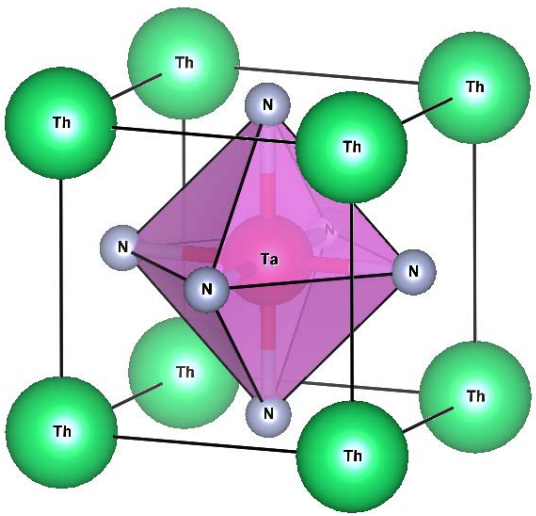
- **Observed a double Dirac cone for the system with the mirror Chern number of 2.**

- **Breaking the surface states by removing crystalline symmetries.**

Tanaka et al. (Tohoku Univ.), Nat. Phys. 8, 800 (2012).
Dziawa et al. (Poland), Nature Mater. 11, 1023 (2012).
Xu et al. (Princeton Univ.), Nat. Commun. 3, 1192 (2012).

- **Okada et al. (Tohoku Univ. & Princeton Univ.) Science 341, 1496 (2013).**
- **Zeljkovic et al. (Boston Univ.), Nature Mater. 14, 318 (2015).**

Cubic perovskite nitride $ThTaN_3$



- ✓ Space group: $Pm\bar{3}m$ (#221) with C_{4v} (mirror +4-fold rotation) sym.
- ✓ Lattice constant of a = 4.02 Å

Brese and DiSalvo,
J. Solid State Chem. 120, 37 (1995).

Interesting Aspects

- Narrow gap semiconductor
- A sizable spin-orbit coupling in Ta ion is expected.
- A rare cubic perovskite nitride: itinerant hole or electron doping is expected to be much easier than in oxides.

[Botana, Pardo, and Pickett, Phys. Rev. Appl. 7, 024002 (2017).]

Calculation Methods

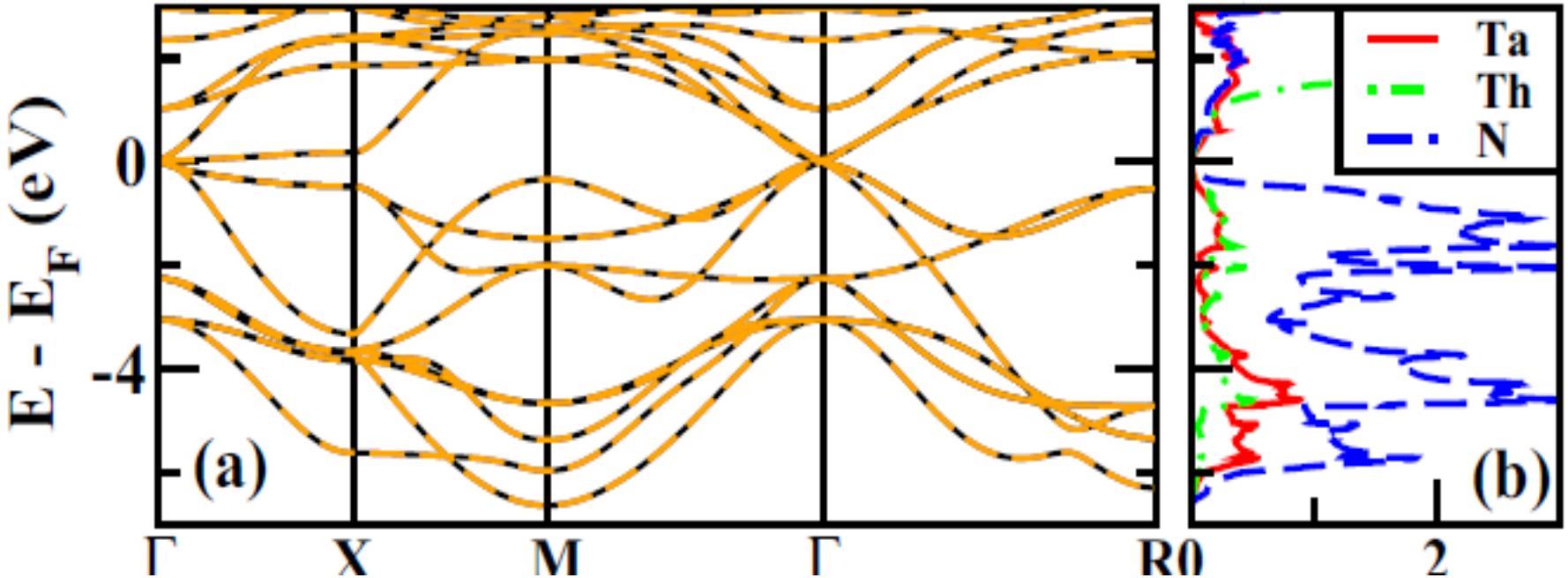
- All calculation results are based on Wien2k.
  - ✓ 21x21x21 *k*-mesh
  - ✓ $R_{mt}K_{max} = 7$
  - ✓ APW radii of Th (2.4), Ta (2.0), and N (1.7) (in units of *a.u.*)
  - ✓ GGA & GGA+SOC

- Wannier function approach (Wannier90)
  - Basis : Ta 5d, N 2p, and Th 6d, 5f

- Surface state calculation
  : WannierTools, based on the Green function method

- Thermoelectric property
  : Boltztrap, based on the semiclassical Boltzmann transport theory with a constant relaxation time approximation
  - ✓ dense k-mesh : 60000 k-points within IBZ

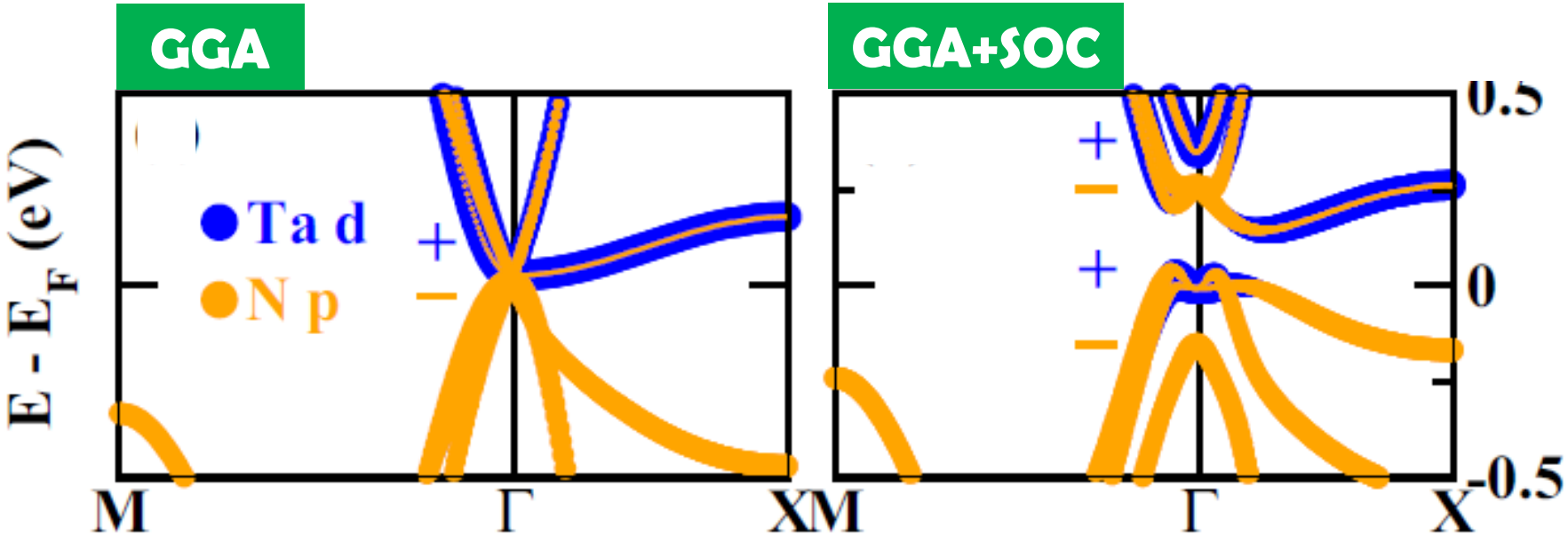
Electronic structures in GGA & GGA+SOC



Brown dashed lines: Wannier representation

- Even in GGA, this system is nearly gapped.
- The top of the valence bands is N 2p, whereas the bottom of the conduction bands is the Ta t_{2g}.

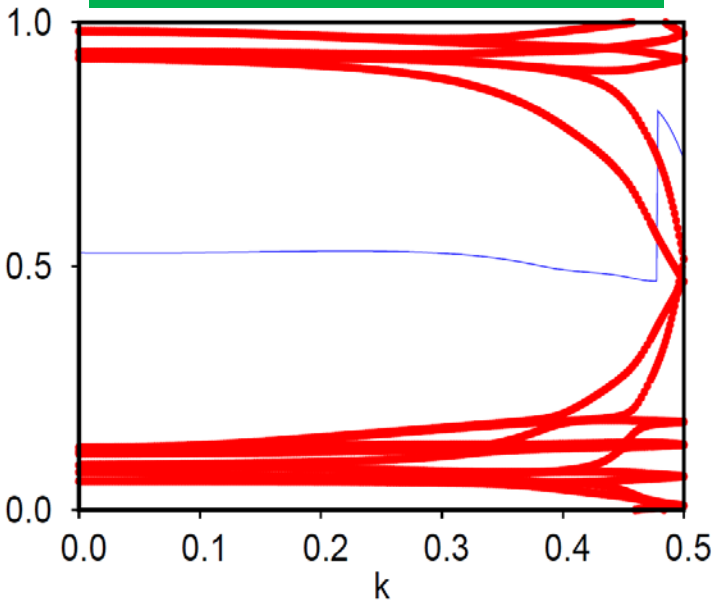
Blowup fatband description



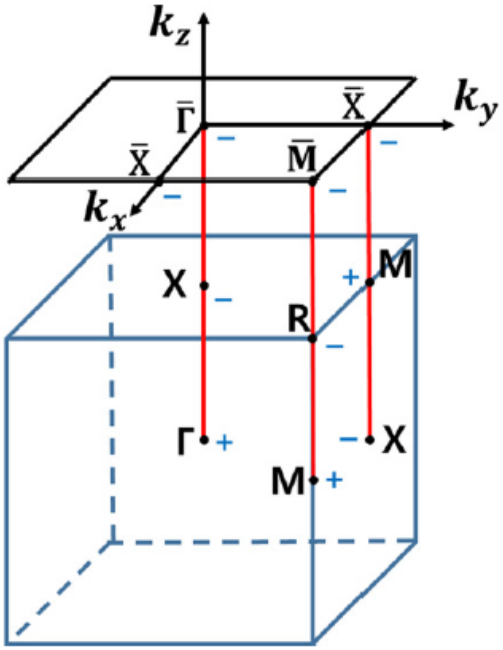
- The Ta d orbitals undergo a substantial spin-orbit coupling (SOC), splitting the 3-fold bands on the either side into a doublet and singlet at the zone center.
- SOC results in band inversion and enhancing the energy of 150 meV.
- This feature suggests a nontrivial topological character.

Z_2 indices & WCC on the (001) surface

Hybrid Wannier Charge Center

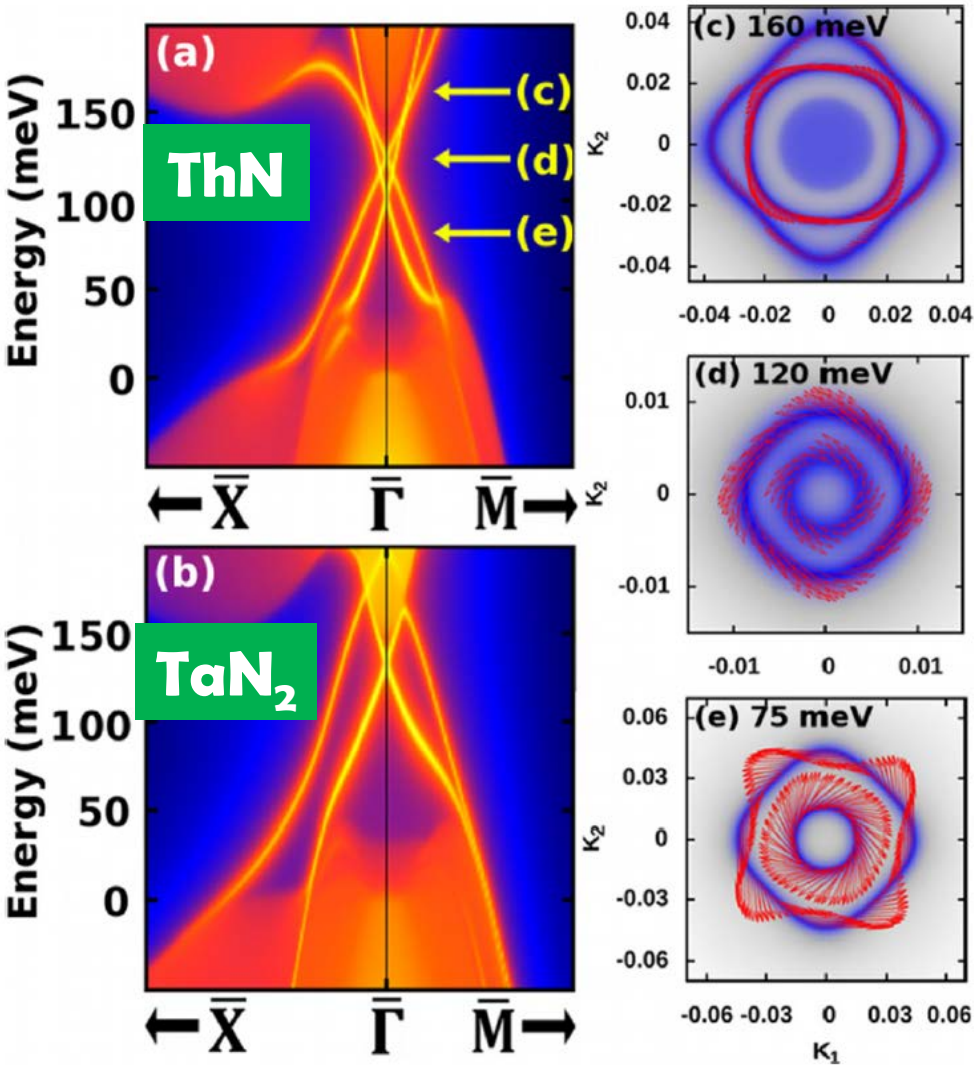


Parity at TRIM



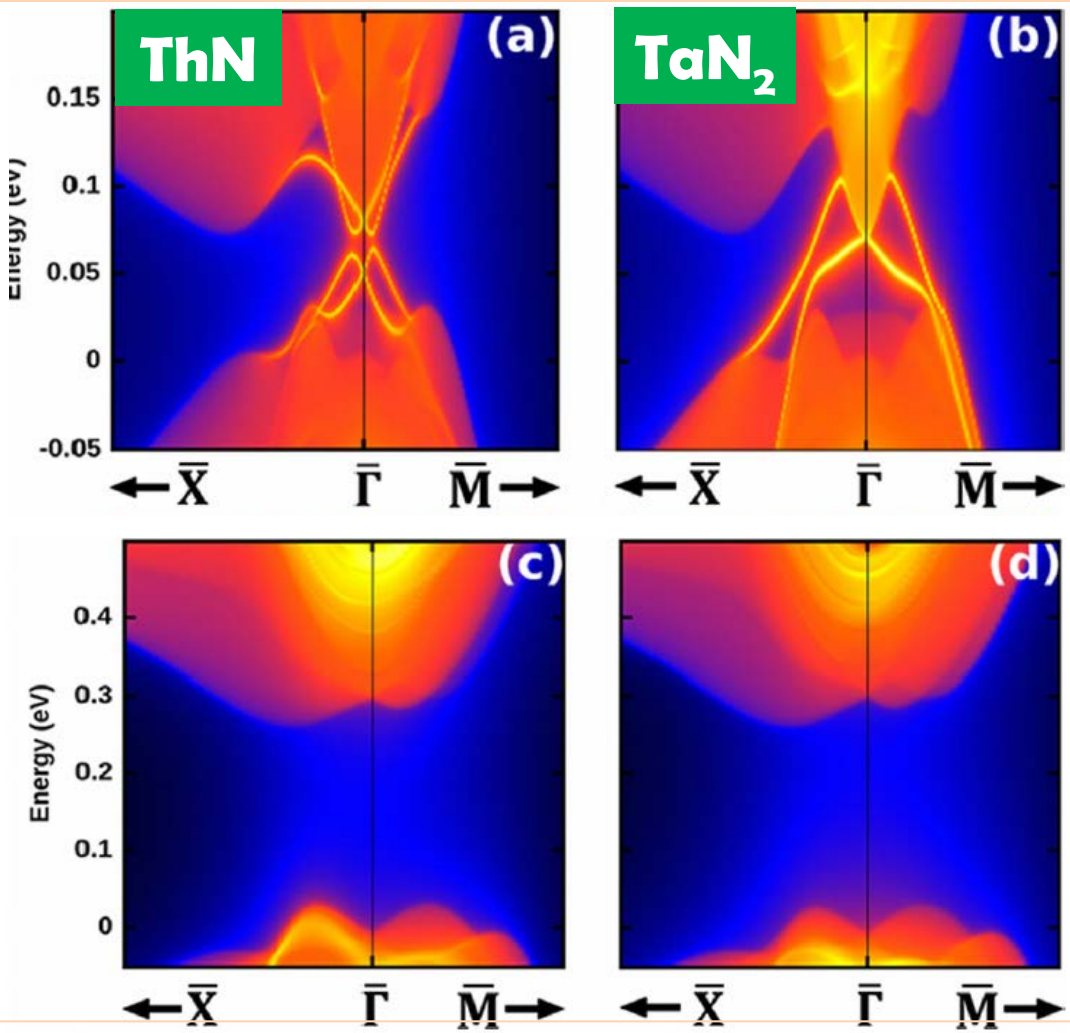
- The HWCC for half of the BZ on the mirror plane shows **an even crossing and trival Z_2 indices 0;(000)**.
- The trivial indices are also obtained from the parties of all occupied bands at the TRIMs.
- **[Question] Is this system topologically trivial?**

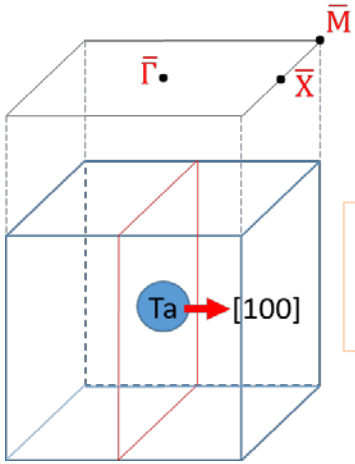
(001) surface spectral function in GGA+SOC



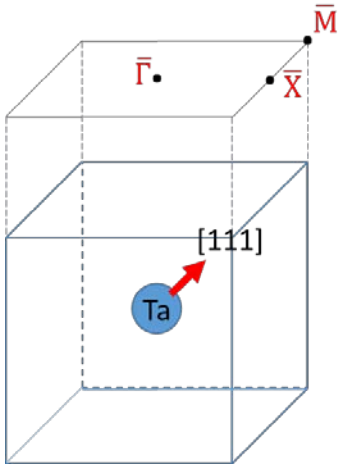
- The function is obtained from the Green function approach.
- In both terminations, **two pairs of surface bands crossing the gap appear at the zone center.**
- The right columns show the spin textures (red arrows) on the cuts of the Dirac cones.

Breaking symmetries





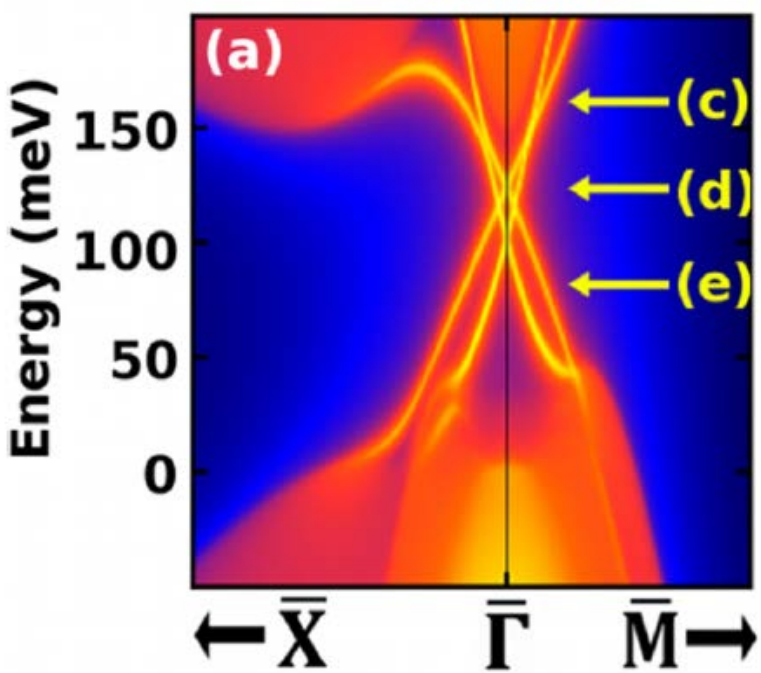
No mirror sym.



No mirror & C4 sym.

- **Breaking both the C_4 rotation and mirror symmetries** removes the surface states completely.

Nature of the topological character



- **The mirror Chern number:**

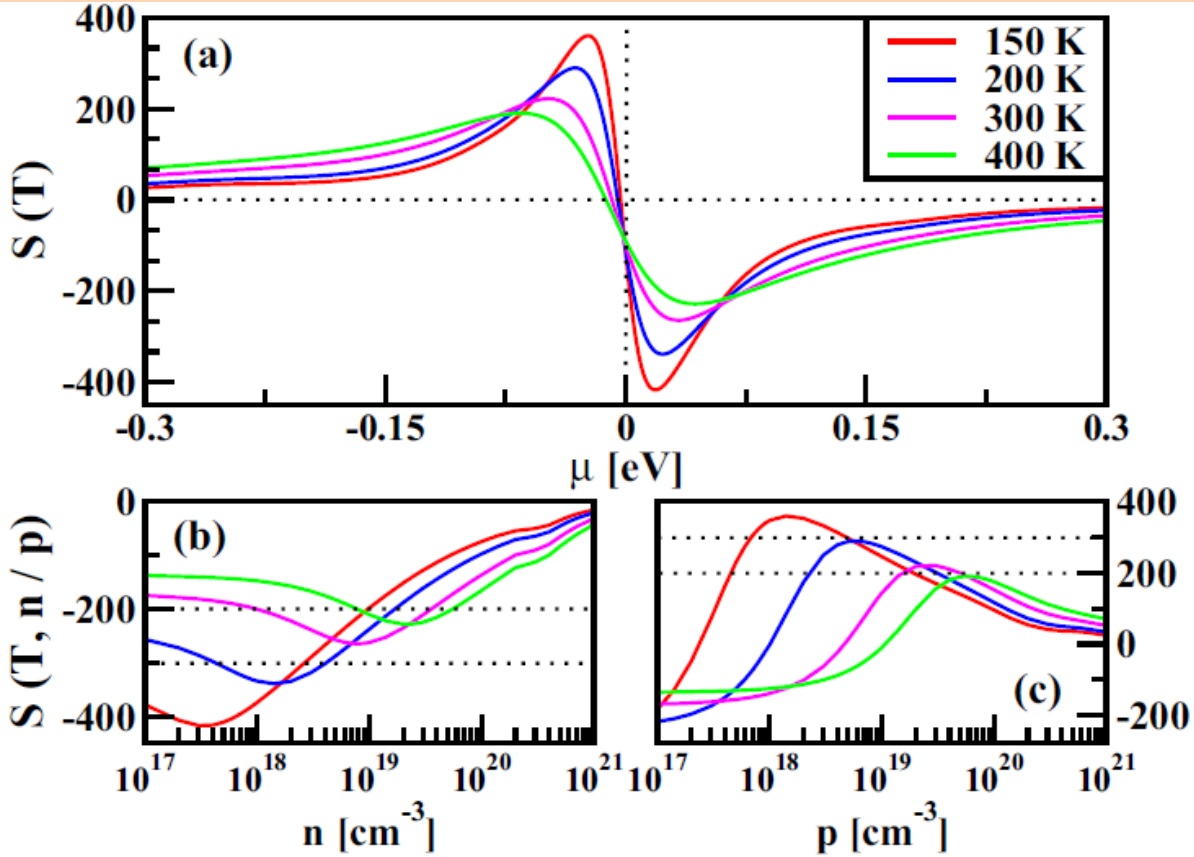
$$|C_M| = \frac{C_{+i} - C_{-i}}{2} = 2$$

for Bloch states with eigen values $\eta = \pm i$.

- **It indicates that this system is a TCI protected by the C_4 rotation + mirror symmetries, as in the antiperovskite.**
- **These two pairs of surface bands indicates the mirror Chern number of 2.**
- **The two Dirac cones concurrently emerge at the zone center.**

Seebeck coefficients S(T) in GGA+SOC

In units of $\mu V/K$



- S(T) is roughly doubled by SOC.
- A very high value of ~ 400 $\mu V/K$ is at 150 K for a small hole.
- For low doping level ~ $10^{-4} - 10^{-6}$ *carriers*/f.u., it retains excellent thermoelectric performance denoted the dashed lines in (b) & (c).

TCI & thermoelectric properties

- **No direction relation between thermoelectric (bulk) and topological (surface) properties**
- ✓ **Only commonality is a narrow band gap.**
- ✓ **SOC leads to considerable changing in dispersion around E_F, thus providing a steep DOS (often signal of large thermopower).**
- ✓ **It happens in this system.**

PRL 112, 226801 (2014) PHYSICAL REVIEW LETTERS week ending 6 JUNE 2014

Enhanced Thermoelectric Performance and Anomalous Seebeck Effects in Topological Insulators

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[2]*ENN Intelligent Energy Group, ENN Science Park, Langfang 065001, China*
(Received 5 February 2014; published 2 June 2014)

Improving the thermoelectric figure of merit zT is one of the greatest challenges in material science. The recent discovery of topological insulators (TIs) offers new promise in this prospect. In this work, we demonstrate theoretically that zT is strongly size dependent in TIs, and the size parameter can be tuned to enhance zT to be significantly greater than 1. Furthermore, we show that the lifetime of the edge states in TIs is strongly energy dependent, leading to large and anomalous Seebeck effects with an opposite sign to the Hall effect. These striking properties make TIs a promising material for thermoelectric science and technology.

- ✓ **The surface conductance leads to an anomalous Seebeck effect that can be tuned by engineering the size and shape of the sample.**
  ⇒ **a new frontier in topological materials.**

Summary

- The perovskite $ThTaN_3$ is a TCI with a large gap of 150 meV and the mirror Chern number of 2.
- $ThTaN_3$ has a large Seebeck coefficient with a maximum value of ~ 400 $\mu V/K$.
- $ThTaN_3$ is not only a TCI, but also displays highly favorable thermoelectric properties.
- It may provide new possibilities for platforms for engineering devices with larger figures of merits.